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**SELECTION OF CATIONS FOR
AMBIENT TEMPERATURE
CHLOROALUMINATE MOLTEN
SALTS USING MNDO MOLECULAR
ORBITAL CALCULATIONS**

John S. Wilkes

Charles L. Hussey

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MOLECULAR ORBITAL CALCULATIONS

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SUMMARY

Mixtures of aluminum chloride and some organic chloride salts form new salts that are liquid at room temperature. The properties of the organic salt often have a large effect on the physical and electrochemical properties of the melts. We describe here a method for predicting the reduction potentials for a variety of organic cations that might be candidates to form low melting mixtures with aluminum chloride. The method involves calculation of lowest unoccupied molecular orbital energies for cations and estimations of half-wave reduction potentials. Comparisons of predicted and measured potentials are made.

PREFACE

This report describes work in progress that is part of a project designed to develop new low temperature electrolytes for battery applications. Calculations and experiments on new cations are continuing and the complete results will be reported at a later date. The experimental portions of this report were performed as part of an AF Reserve project by Capt Hussey.

INTRODUCTION

Molten salt electrolytes for primary and secondary battery cells have been the subject of intense interest in recent years. In a search for low melting salts we have studied mixtures AlCl_3 and alkali halides (1-3), and, more recently, mixtures of AlCl_3 and 1-alkylpyridinium halides (4,5). Some examples of the 1-alkylpyridinium chloroaluminates are liquids at room temperature and have been examined in detail by us and others (6). One attractive feature of these ambient temperature melts is that the basicity, as expressed by Cl^- concentration, is controllable over a very wide range. This is important, since the chemistry of solutes is greatly affected by the melt basicity.

Osteryoung showed that a basic chloroaluminate melt using the 1-butylpyridinium cation will react with aluminum electrodes (7). This implies that batteries using such an electrolyte would be constrained to using anodes less active than aluminum. Gale (8) and we (9) have shown that the reaction that limits the use of active metal electrodes is reduction of the alkylpyridinium cation, followed by coupling to produce 1,1'-dialkylbipyridyls. The reaction with aluminum in the basic melts may be avoided only by substituting for the alkylpyridinium a cation that has a reduction potential more cathodic than $\text{Al(III)} + 3\text{e}^- \rightarrow \text{Al}^0$ in the melt.

We report here a method by which alternate cations for chloroaluminate melts may be screened using calculated electron affinities. We also report experimental verification of the usefulness of the method.

EXPERIMENTAL

Calculation of LUMO energies were made using the MNDO program kindly provided by M. J. S. Dewar. The program was run on a Burroughs 6700 or a Digital Equipment Corp. VAX computer.

The alkylpyridinium chlorides (10) and dialkylimidazolium chlorides (11,12) were prepared by methods described previously. Tetramethylformamidine chloride was prepared exactly as reported by Kantlehner and Speh (13).

Reduction half-wave potentials were obtained in DMF containing 0.1 M tetrabutylammonium perchlorate at a rotating disc electrode (1500 RPM). Potentials were measured at 25°C versus a saturated calomel electrode isolated from the bulk solution via a Vycor tipped bridge tube. The solution was presaturated with and maintained under a blanket of dry nitrogen gas.

RESULTS AND DISCUSSION

The energy of the lowest unoccupied molecular orbital (LUMO) is obtained directly from the MNDO molecular orbital calculation. The LUMO energy calculated by the MNDO method is the gas phase electron affinity (EA) of the molecule (14). Furthermore, the solution reduction potential may be calculated from the electron affinity, the differential solvation energies and a constant characteristic of the reference electrode (15). Since the cations being considered are all similarly sized, the differences in solvation energies were neglected and a direct correlation between LUMO energies and $E_{1/2}$ potentials was made as shown in equation 1.

$$E_{1/2} \text{ (reduction)} = EA + C \quad (1)$$

The large diversity and numbers of organic compounds makes an exhaustive screening of prospective cations an overwhelming task. In this study the types of organic cations considered were limited to those where the positive charge was accommodated by a quaternary nitrogen. Two such classes of cations that have been useful in electrochemical systems are the tetra-alkylammonium ions, often used in supporting electrolytes, and the 1-alkylpyridinium ions.

The ability of the 1-alkylpyridinium chlorides to form ambient temperature molten salts in combination with AlCl_3 provided good precedent to investigate other cations based on pyridine. Table I lists some pyridine based cations. Compounds II-IV have a single variable length alkyl substituent on the ring nitrogen. The remaining cations have a methyl group on the nitrogen and one to three methyl substituents the ring carbons. Compounds VI-VIII have one additional methyl, IX has two additional methyls and X has three additional. The LUMO energies calculated for all of the 1-alkylpyridinium cations fall into a rather narrow range. This is somewhat surprising, since the presence of electron inducing substituents on the pyridine ring might be expected to help stabilize the positive charge, therefore decreasing the LUMO energy and shifting the $E_{1/2}$ cathodically. Although X has the lowest LUMO energy, it is only 0.09 eV lower than the much studied V, which is easily reduced by aluminum in basic melts.

Many quaternary nitrogen cations not based on pyridinium may be envisioned. Table II lists some cations that were screened for their possible resistance to reduction by calculating LUMO energies. The aromatic 6-membered heterocycles having two ring nitrogens (XI-XIII) were predicted to be more easily reduced than the alkylpyridinium

cations, thus they were poor candidates for providing melts with a lower cathodic limit. The aromatic 5-membered heterocycles having two ring nitrogens (XIV-XVIII) have LUMO energies significantly lower than the pyridinium based cations. The LUMO energies for the amidine (XIX, XX) and guanidine (XXI, XXII) based cations are also lower.

The dialkylated imidazoles have calculated electron affinities about 0.9 eV lower than a typical N-alkylated pyridine, implying a like magnitude shift in reduction potentials. Comparison of the measured $E_{1/2}(\text{red})$ values for V and XVI shows a cathodic shift of 0.80 V, very close to that predicted by the MNDO method. A decrease in the reduction potential of that magnitude would make the cathodic limit more negative than an aluminum reference in a melt comprised of a mixture of AlCl_3 and excess 1,3-dialkylimidazolium chloride.

Figure 2 illustrates the correlation between the calculated LUMO energies and measured half-wave reduction potentials for some of the compounds in Tables I and II. The correlation supports linear relationship predicted by equation 1, although the scatter is quite substantial. The 1,2-dimethylpyrazolium cation (XIV) is a puzzling case. The predicted reduction potential for that cation is about -1.6V vs SCE. The chloride was prepared and the measured reduction was found to be -2.24V vs SCE. This is the most negative value of any of the heterocyclic chlorides prepared to date, and merits further investigation as a component of a chloroaluminate molten salt. The fact that the extraordinarily negative reduction potential of (XIV) was not predicated by the MNDO method demonstrates that the

calculations can only be used as a general guide, and that exceptions may be expected. The pyridinium cation (I) may or may not be well correlated. A very wide range of measured $E_{1/2}$ (reduction) values have been reported in the literature, and are shown as a bar in Figure 2. The variation is probably due to differences in solvent, counter-ion, or method of determination.

The geometry optimization feature of the MNDO program proved valuable in two cases where the concept of electronic induction alone would have given the wrong answer. Usually, the substitution of methyl groups for hydrogen atoms in cations significantly decreases the electron affinity, thus making the reduction potentials more negative. This is demonstrated in Table III, where XXV is lower than XXIV and XXIX is lower than XXVIII. The effect is due to stabilization of the positive charge in the cation by the electron inducing effect of the methyl group, and the predicted behavior is well substantiated experimentally for XXV, XXIV, XXIX and XXVIII. As expected, XXVII is predicted to have a more negative LUMO energy than XXVI. It was surprising initially when XXXI was calculated to have a higher (less negative) LUMO energy than XXX. The explanation is clear when the MNDO predicted geometries are examined, as shown on Figure 2. The presence of six methyl groups in XXXI, while electronically favorable, sterically prevents the delocalization of charge among the three nitrogen atoms. If one methyl group is removed from each nitrogen as in XXXII, the geometry flattens and delocalization should be allowed. This is verified in Table III for compound XXXII, where the trimethyl substituted cation does have a more negative LUMO energy than the non-methyl substituted parent (XXX).

CONCLUSIONS

Molecular orbital calculations may be used to estimate the reduction potentials of a variety of organic cations. This information may be used to select promising cations for the preparation of chloroaluminate melts, where the cation will not react with active metals in the basic region. Cations based on imidazole were calculated to have sufficiently low reduction potentials that they are attractive candidates for chloroaluminate melts. The method cannot predict physical properties; however, cations similar in size to the previously studied 1-alkylpyridinium cations might also be expected to form ambient temperature melts .

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We wish to thank Dr. M. J. S. Dewar for providing the MNDO program, Dr. Larry P. Davis for assisting in the application of MNDO in our systems and Dr. Melvin Druelinger for his help in the synthetic aspects of the study.

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TABLE I
Pyridinium Based Cations

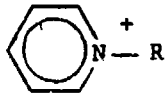
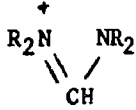

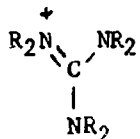
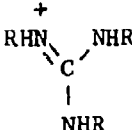
<u>Cation</u>	<u>-LUMO Energy</u> <u>(eV)</u>	<u>E_{1/2} (red)</u> <u>(V)</u>
pyridinium (I)	6.01	-0.472
1-methylpyridinium (II)	5.84	-1.28
1-ethylpyridinium (III)	5.75	-1.34
1-propylpyridinium (IV)	5.72	-1.15
1-butylpyridinium (V)	5.70	-1.209
1,2-dimethylpyridinium (VI)	5.74	
1,3-dimethylpyridinium (VII)	5.76	
1,4-dimethylpyridinium (VIII)	5.76	
1,2,4-trimethylpyridinium (IX)	5.71	
1,2,4,6-tetramethylpyridinium (X)	5.61	
1-butyl-4-(dimethylamino)pyridinium (XXXI)		-1.824

TABLE II
Non-pyridinium Based Cations

<u>Cation</u>	<u>-LUMO energy (eV)</u>	<u>E_{1/2} (red) (V)</u>
1-methylpyridazinium (XI)	6.30	
1-methylpyrimidinium (XII)	6.23	
1-methylpyrazinium (XIII)	6.03	
1,2-dimethylpyrazolium (XIV)	5.31	-2.24 ¹
1,3-dimethylimidazolium (XV)	4.86	-1.981
1-methyl-3-ethylimidazolium (XVI)	4.78	-2.007
1-methyl-3-butylimidazolium (XVII)	4.70	-2.001
1,2,3-trimethylimidazolium (XVIII)	4.83	
formamidinium (XIX)	5.55	
tetramethylformamidinium (XX)	4.89	-1.83
guanidinium (XXI)	4.81	
hexamethylguanidinium (XXII)	4.95	
tetramethylammonium (XXIII)	4.37	

¹near decomposition limit of solvent

TABLE III

	Compound (R = H)	-LUMO energy (eV)	Compound R = CH ₃	-LUMO energy (eV)
	XXIV	6.01	XXV	5.84
	XVI	5.55	XXVII	4.89
	XXVIII	4.94	XXIX	4.37
	XXX	4.81	XXXI	4.95
	XXX	4.81	XXXII	4.47

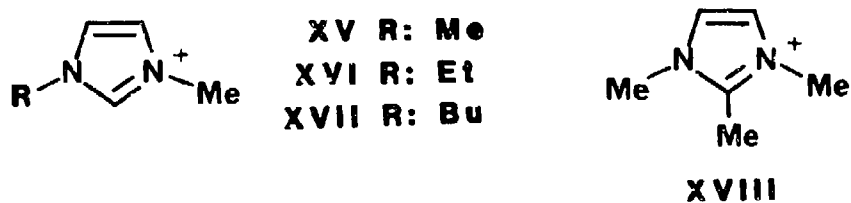
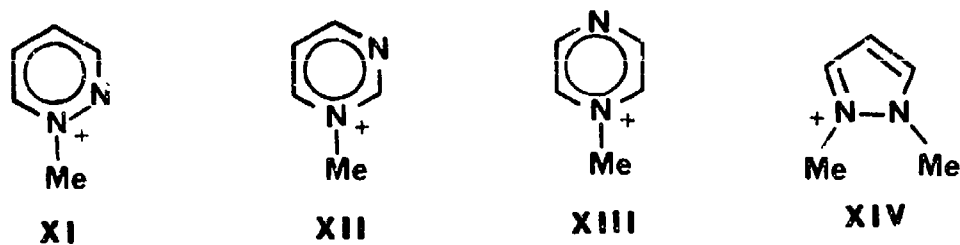
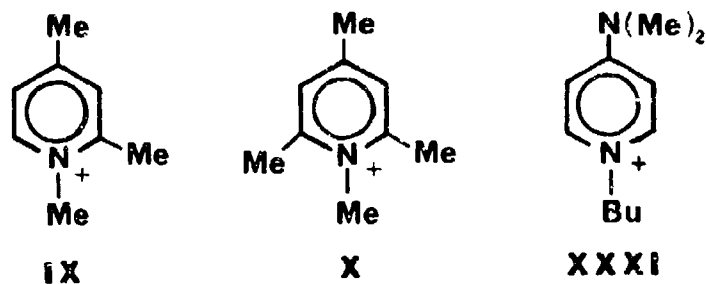
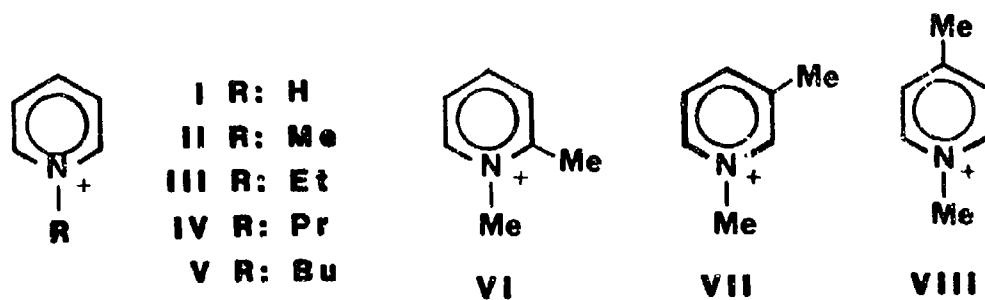
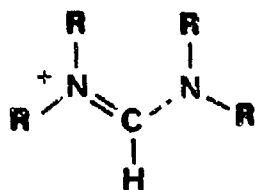
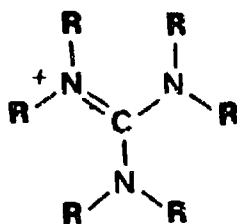


FIGURE 1
Cation Structures



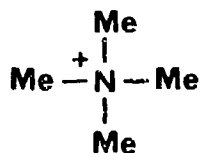
XIX R: H

XX R: Me



XXI R: H

XXII R: Me



XXIII

FIGURE 1 (Continued)

Cation Structures

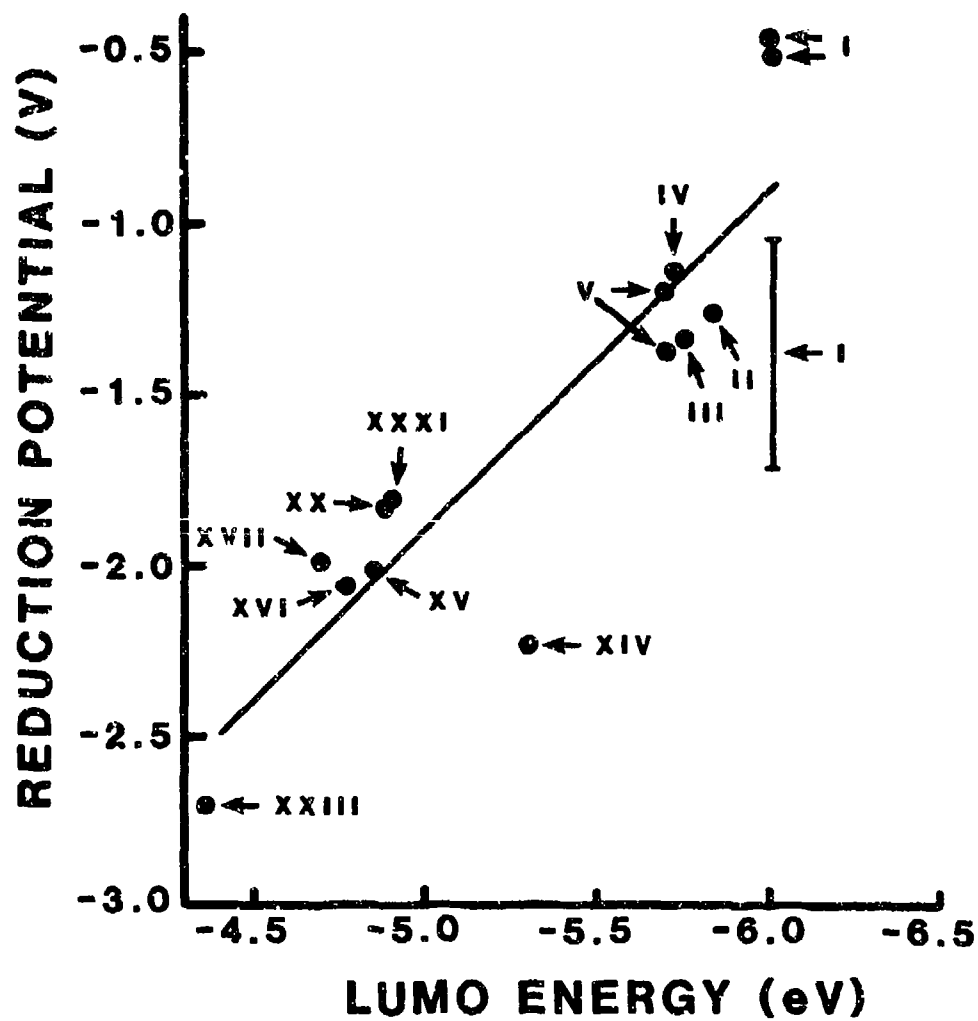


FIGURE 2

Correlation of LUMO Energies and Solution Reduction Potentials

ABBREVIATIONS AND ACRONYMS

LUMO	Lowest Unoccupied Molecular Orbital
MNDO	Modified Neglect of Diatomic Overlap
DMF	dimethylformamide
RPM	revolutions per minute
$E_{1/2}$	half-wave potential
eV	electron volt
V	volt
SCE	standard calomel electrode
EA	electron affinity